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(54) METHOD OF PRODUCING PLASTICS FOAMED ARTICLES

(71) We, THE FURUKAWA ELECTRIC COMPANY LIMITED, a Japanese Company, of No. 6—1, 2-chome, Marunouchi, Chiyoda-ku, Tokyo, Japan, and NISSEI KOGYO KABUSHIKI KAISHA, a Japanese Company, of No. 1566, Kasuga, Maikata-shi, Osaka-fu, Tokyo, Japan, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement: —

Plastics foamed articles have been used very widely recently as building materials and packaging material and for other purposes because they are light in weight and low in cost, in addition to their excellent heat insulating property and shock and sound absorbing characteristics.

However, the shortcoming of plastics foamed articles lies in their low mechanical strength as compared with unfoamed plastics articles. If this shortcoming can be overcome, their use will be further expanded. In an attempt to improve and enhance the mechanical properties of foamed plastics articles which are inferior as mentioned above, there is a method of forming a thick, strong surface layer on foamed shaped articles, and the foamed shaped articles having such surface layers formed thereon are not only strong but also have features which are peculiar to plastics foamed articles. Thus they are very useful.

A method of producing such foamed plastics articles having surface layers (as shown in U.S. Patent 3,455,483 and Japanese Patent Publication number 46—10316), has been employed in which first an unfoamed surface layer is formed on the inside wall of a mould, then a foamable plastics compound is placed in the same and is heated for foaming. While shaped foamed articles having surface layers can be produced by this method, it is necessary in this production method to charge material twice into a mould, and heating is required every time the material is charged, thus involving high cost, and at the same time there is some difficulty in forming a complete bond between the surface layer and inner layer.

As a method of producing plastics shaped articles having surface layers and foamed inner layers by a one-step moulding, there is as shown in U.S. Patent 3,052,927, a rotating moulding method employing centrifugal force, in which a material such as polyurethane is used. In this method of foam-moulding of polyurethane, or the like, since foaming is performed whilst a mould is rotated at a high speed, foaming starts from such portions as are distant from the axis of rotation. Therefore, the density within moulded articles thus obtained varies gradually from one direction to the other. This method also requires expensive equipment for high speed rotation, and furthermore has the shortcoming of difficult foaming because the visco-elasticity of polymers at the time of foaming is very high in a foamable compound of thermoplastic resin.

On the other hand, U.S. Patent 3,542,912 prescribes a method in which polymers of low melting point and those of high melting point are placed in a mould and are heated, whilst being rotated, so that the polymers of low melting point form an outer layer while those of high melting point form the inner layer. This method is limited to polymers which are not compatible with each other, and, as the polymers of low melting point constitute the outer layer, the moulded articles so obtained are inferior in heat resistance, and similar characteristics.

The inventors have carefully studied in detail the method for producing foam-moulded articles having such a composite structure as mentioned above, and found that when a powdered plastics material, and a granular plastics material containing a foaming agent, which granular plastics material has a larger particle size than the powdered plastics, are placed in a mould and heated while the mould is rotated slowly at such a speed as produces virtually no centrifugal effect, firstly the powdered plastics material adheres to the entire

inner surface of the mould to form a surface layer, and then the granular plastics material adheres to that surface layer. Since a comparatively large amount of foaming agent is blended into the granular plastics material before hand, this is foamed to fill up the mould, thus producing foamed composite articles with a double structure of a strong and thick surface layer and a well foamed inner core.

The invention accordingly provides a method of producing foamed composite articles which comprises placing in a mould powdered plastics material the particles of which are less in size than 10 mesh, and granular plastics material the particles of which are greater in size than 10 mesh, which granular plastics material contains a foaming agent, the size of the granular plastics particles being at least three times that of the powdered plastics particles, rotating and/or vibrating the mould to separate said two kinds of plastics particles from each other, and heating the same.

Throughout the Specification the mesh sizes quoted refer to standard U.S. sieves.

The shape of the two kinds of plastics particles is not important, and each kind may be pellet-shaped, cubic, spherical, or any other convenient shape. Any of these shapes may be selected so long as there is a sufficient difference in particle size between the two kinds of material. The granular plastics material must have a particle size (in terms of diameter for spherical particles) at least three times greater, and preferably ten times greater, than the particle size of the powdered plastics material.

In this method the two kinds of plastics particles are charged into the mould together and separated by rotation of the mould into a surface layer and a well-foamed inner core due to the difference in particle size of the powdered plastics material and granular plastics material. As the separation into the surface layer and inner core occurs during the plastics melting process, it has nothing to do with the molten viscosity of the plastics, and thus not only thermoplastic resins, but also certain kinds of thermosetting polymer can be used for the surface layer.

Furthermore, in the method of the present invention, such additives as, for example, flame retarding agent, antioxidant, ultraviolet ray absorbing agent, anti-static agent, or powdered or fibre-shape reinforcing agent, can be used in the surface layer only, thereby saving in the amount of expensive additives used.

Thus, the present invention provides a method for the production of composite foamed articles using any plastics having differing characteristics, and its application covers a wide field with very high industrial value.

By the method of the present invention light and strong pellets, and the like can be made which may comprise a surface layer of high density polyethylene, polypropylene, ABS resin, nylon, poly-carbonate, and the like, and an inner core of cross-linkable polyethylene having good foaming characteristics.

Also, a large quantity of hollow glass spheres, lightweight aggregate, and the like, can be added, in addition to the powdered plastics and the foamable plastics, whereby composite articles can be produced having a foamed plastics inner core containing hollow glass spheres, or light weight aggregate, and a surface layer. Such composite articles have excellent heat-resistance and are useful as heat-insulating materials.

The present invention also makes it possible to obtain moulded articles which contain plastics scrap mixed in their inner-core, which is covered by the surface layer, the plastics scrap being first pulverised to the size of the granular plastics (i.e. greater than 10 mesh).

It is also possible according to the present invention to produce such foamed shaped articles having three or more layers (for example, as well foamed innermost layer or core, an unfoamed layer, and a slightly foamed outer layer) by placing into a mould, plastics material with three different particle sizes, consisting of very fine powdered plastics material which is slightly foamable, granule-shaped plastics material which is well foamable and coarse powder of plastics material having such a particle size as is intermediate between the fine powdered plastics and the granular plastics, and then heating the same. It is also possible to secure a very strong bond between the surface layer and the inner core by suitably selecting the above-mentioned intervening plastics material.

The powdered plastics used in the present invention may be any thermoplastic resin, thermosetting resin in such a state that it is not completely cured and has some melting tendency remaining, or powder or thermoplastic materials of a cross-linkable nature, or it can be a blended mixture of any of these materials. The cross-linkable plastics material mentioned above can be plastics material having such chemical cross-linking agent added thereto as organic peroxide, azide cross-linking agent, or the like, or plastics material partially cross-linked beforehand by a chemical cross-linking agent or by an irradiation process, or the like, only to such an extent that it will still flow satisfactorily.

As stated above, the powdered plastics used in the present invention needs to be smaller in particle size than the granular foamable plastics, so that the powdered plastics can be melted and made to adhere to the inner surface of a mould sooner than the granular plastics while being moved within the mould. However, if the powdered plastics are too fine, as the mould is rotated this fine powdered plastics material is apt to coagulate and

becomes difficult to move within the mould; therefore it becomes difficult to separate the fine powdered plastics and the granule plastics from each other and a surface layer with uniform thickness cannot be obtained.

Thus, the particle size of the powdered plastics in the present invention should be determined according to the kind of powdered plastics, structure of mould, and the particle size of granular plastics, and should be less than 10 mesh and preferably less than 30 mesh. As the powdered plastics must adhere to the inner surface of the mould sooner than the granular plastics, it is also desirable that the powdered plastics should be more easily softened than the granular plastics. However, since two kinds of material with different particle sizes are used in the present invention it is not necessarily mandatory to select such powdered plastics as are easier to soften than the granular plastics. For example, by using polypropyrene with a melting point of 160°C as the powdered plastics material, and high-density polyethylene as the granular material, satisfactory moulded articles, for which the present invention is intended, can be obtained. As the powdered plastics material must be easily moved and dispersed within a mould, such powdered plastics as are produced by sedimentation out of solvent are preferred to those produced by mechanical pulverisation. In some cases two kinds of powder, of 200 mesh and 30 to 50 mesh, are blended to ensure well-balanced movement and easy melting. As another method of enhancing the movement within a mould, a powdered metal, which has good thermal conductivity and a higher density than that of powdered plastics, may be added. This powder may be simply blended into the plastics material mechanically, such as by a blender, and a preferred material, for enhancing movement in the mould is powdered aluminium.

One of the purposes of the present invention is to obtain strong and light weight foamed plastics shaped articles having strong surface layers. Therefore, for the powdered plastics in the present invention, such rigid type materials as polypropylene, high density polyethylene, nylon, ABS resin, rigid polyvinyl chloride resin, polycarbonate, or phenolic resin are preferably used. Among these materials, moulded articles having surface layers of polyvinyl chloride resin and phenolic resin have flame-retardant characteristics, and are therefore useful especially for building materials and transportation gears. Also, from the standpoint of flame-retardance, a large amount of non-organic powder or fibre-shape additive may be added to the surface layer. As the surface layers of the present invention should be strong, they are not much foamed, and even when they are foamed, the foaming is normally limited so that the cells retain a spherical shape. However, in the case of moulded articles for transportation gears it is sometimes desirable that they should have a soft surface, and in some cases a larger amount of foaming agent is added to the powdered plastics to form larger polyhedral, cells in the surface layer. In such a case, powdered plastics of a cross-linkable nature is preferably used, and it is especially desirable to knead the chemical cross-linking agent or foaming agent into the plastics using a roll or an extruder and thereafter to pulverize the mixture into fine powder. When cross-linkable thermoplastic resin is used as the powdered plastics, the shock resistance of the moulded articles will be improved, the amount of materials flowing out of the mould will be reduced, and when a mould having a patterned inner surface is used, an attractive pattern can be formed on the surface of the moulded articles obtained. The surface layer in the present invention ordinarily has a thickness of 0.5 to 15 mm., while the thickness of 2 to 7 mm. is desirable.

The granular plastics used in the present invention may be any thermoplastics material having flowability when the foaming agent decomposes or evaporates, or a mixture of such plastics and of natural or synthetic rubber which is compatible with said plastics may be used. Materials which are particularly suitable for the granular plastics are low-density polyethylene, rigid PVC, polystyrene and/or nylon. In any case the granular plastics material used in the present invention must have a larger particle size than that of powdered plastics. Thus, it must be of 10 mesh size or larger, and preferably it is of 5 mesh size or larger, and from the stand point of ease of separation from the powdered plastics during rotary moulding within a mould it should preferably be of spherical shape or of similar shape, but it may be of cuboid or of rectangular parallelepiped shape. Furthermore it may be of any irregular shape as is obtained simply by mechanically pulverising the plastics material. Composite articles may be produced using any weight ratio of powdered plastics material to granular plastics material, but usually the weight ratio of powdered plastics to granular plastics is from 1:4 to 9:1. The foamed shaped articles of the present invention should desirably have a well foamed core, and for that purpose cross-linkable plastics is used in many cases. When non-cross-linkable powdered plastics and cross-linkable granule plastics are placed in a mould and are heated, the powdered plastics are melted and form the surface layer, then the cross-linkable granular plastics cross-link and foam, and as the cells within this material are very stable and it is difficult for the generated gas to escape, a sufficiently high inner pressure is generated within the mould, thus producing moulded articles having good outer appearance, stable shape and excellent

mechanical strength. Also the surface layers of such moulded articles have very uniform thickness and are well bonded with the inner core.

Hollow glass spheres, light weight aggregate, wood chips, non-foamable plastics materials, plastics mixture, and the like may be added to the powdered plastics and granular plastics to produce moulded articles having a core of foamed material, hollow glass spheres and other constructions. By suitably selecting these materials, heat-resistance, strength and buoyancy, or other desired qualities may be imparted to the article. Plastics scrap often contains materials such as wood chips, metal chips, sand, etc., but the moulding method of the present invention can produce moulded articles containing such material in their inner core, and therefore it is very desirable as a means of utilising such plastics scrap. When slightly foamable powdered plastics, well foamable granular plastics, and coarse powder, which does not foam and has such a particle size intermediate between those of powdered plastics and granular plastics, are placed together into a mould and heated while being rotated, foamed shaped articles having three layers, namely a well foamed innermost core, a non-foamed layer, and a slightly foamed outer layer, can be produced. As such moulded articles have light weight and high strength and shock resistance, they are most suited in many cases as material for use in the interior of automobiles. By suitably selecting the intervening plastics, the bonding between surface layer and inner core can be enhanced when the plastics material used for the surface layer has little or no compatibility with the plastics material used for the inner core.

The foaming agent in the present invention should have a decomposition temperature higher than the softening temperature of the plastics, and it may be an organic foaming agent or an inorganic foaming agent. Sometimes a volatile foaming agent may be used. While the foaming agent used with powdered plastics is usually blended thereinto by a blender, the foaming agent mixed into foamable granule plastics is ordinarily mixed therein by a roll mill or an extruder.

When a cross-linking agent is used, it is normally desirable to cross-link the plastics material first, and then thereafter to foam it. Therefore, the decomposition temperature of the foaming agent used should ordinarily be higher than the decomposition temperature of the cross-linking agent. The moulded articles in the present invention ordinarily have surface layers expanded to from one to three times their unfoamed volume and inner cores expanded to from 5 to 30 times their unfoamed volume, and the complete moulded articles has a volume from 2 to 10 times greater than that unfoamed starting materials.

The mould used in the present invention will be of such a type as can be closed, but it need not necessarily be completely airtight. However in order to secure an attractive external finish, while keeping the density of the moulded articles is low, the internal pressure in the mould at the time of foaming is desirably high. Any ordinary cast metal mould can be used, and a mould made by bending steel plates or by welding can also be used. The surface layers of the foamed shaped articles of the present invention are formed as heat is transmitted from the outside of the mould by thermal conductance into the mould and the powdered plastics material is first molten by the heat. Therefore when a surface layer of uniform thickness is desired the mould can be uniformly heated. However there may be a case in which some portion of the article needs to be made strong and it is desirable to provide a thicker surface layer for that portion. Then such portion of the mould as corresponds to the above-mentioned portion is made of a metal having a better thermal conductance, or is made of thinner metal, than the remainder of the mould. In some cases uneven spots may be formed on the inner surface of the mould so that the powder plastics will gather at such spots, or metal screen or lath board may be provided on the inner surface of the mould to reinforce the surface layer portion and at the same time to provide a thicker surface layer. In the present invention it is necessary to make the powdered and granular plastics move within the mould before foaming; therefore there must be an unfilled space of 10%, or preferably more, in the mould. However, when rotation is performed mono-axially, if the unfilled space in the mould exceeds 50%, the surface layer is difficult to form at the portion of the mould adjacent the axis of rotation.

If, while the mould in the present invention is ordinarily heated while being rotated, the rotation is so fast as to cause a centrifugal effect, the separation between the powdered plastics and the granular plastics becomes incomplete. Therefore, the suitable range of rotation speed differs according to the nature, size, and specific gravity of the powdered plastics and granular plastics used and according to the size of mould. The rotation speed is desirably such that the speed of that portion of the mould that moves fastest is ordinarily 15 metres/minute or slower, and preferably from 5 metres/minute to 0.1 metres/minute. This rotation may be performed mono-axially, but may also be performed multi-axially. Generally speaking, it is desirable to make it multi-axial rotation so that the plastics can uniformly contact the entire inner surface of the mould for the purpose of making the thickness of the surface layer uniform. Although in the production method of the foamed shaped articles accord-

ing to the present invention, heating and foaming are performed while the mould is rotated, this is not the only method. Vibration or impact may be given to the mould in combination with rotation or independently thereof to separate the powdered plastics and granular plastics. When vibration or impact only is used, moulded articles are made which are well foamed on one side and not foamed on the other side, and such moulded articles may be used as back supports for chains and in transportation gears. The heating in the present invention is ordinarily performed by hot air or steam. When steam is used it is possible to make the heating temperature low and heating time short; thus steam heating is desirable. The steam heating is also effective in preventing deterioration of the plastics or mould. For the satisfactory separation of powdered plastics and granular plastics within a mould, it is desirable to increase the temperature of the mould rapidly so that the bulk of the plastics material is at a lower temperature, only the powdered plastics material adjacent the mould walls fuses and adheres to the inner surface of the mould to form the surface layer.

When a mould for making a pipe shaped plastics moulded article is heated in an ordinary manner by hot air, a thick surface layer is formed on the outside of the pipe, but is difficult to form the layer on the inner surface of the pipe. However, a funnel-shaped metal fitting may be attached to both ends of the mould to send a greater amount of hot air to the inner tubular section of the mould, or that section of the mould may be made thinner, or a metal having good heat conductivity (such as aluminium) may be used for that section. The heating temperature will ordinarily be from 160 to 400°C and the heating time will be in a range of from 15 to 120 minutes. The cooling of the moulded articles in the present invention will ordinarily be performed rapidly, and usually the mould will be dipped in a water tank to be rapidly cooled by spraying water onto the mould. Since very fine crystals are obtained and escape of gas generated can be prevented by rapid cooling, strong moulded articles can be obtained. While the mechanical strength of the foamed shaped articles of the present invention is generally very high, as they have a strong and thick surface layer, the resistance to compression in the centre of the article tends to be lower as the inner layer is well foamed. In order to enhance further the compression resistance of such foamed shaped articles, substantially round or rectangular shaped depressions may be intentionally formed on the surfaces of the moulded articles. In this way a strong and thick surface layer is formed at the depressed portion, and rigid material, such as a concrete block or piece of wood can be inserted into the depressed portions. When a reinforcing member such as metal plate, shaped steel, pipe, wire, metal screen, lath board, is inserted in the surface layer of a moulded article, which may be either slightly foamed or not foamed, the strength of the moulded article is also remarkably enhanced.

As a method for further enhancing the strength of the foamed shaped articles of the present invention, granules of non-foamable, or only slightly foamable (to from 1 to 3 times their unfoamed volume), plastics material may be added, besides, powdered plastics and foamable granules plastics, and are heated. By doing this, a structural element which is not well foamed is formed in the foamed core and linked to the strong surface layer which covers the entire surface of the plastics moulded article; thus the strength is further enhanced. In some cases this reinforcing plastics material is integrally bound with foamable plastics material beforehand and is used as such. For example, two sheet shaped materials are laminated together and then pulverised and used to form the inner core. Alternatively, foamable granular plastics are formed into a thin rod shape which is then covered with a non-foaming reinforcing layer. This may then be cut up and used as a starting material.

Thus the plastic moulded articles of the present invention have light weight and excellent mechanical properties. Therefore they are very useful as plastics foamed shaped articles of large size such as pallets and other desired articles and their industrial value is very high.

Examples of the present invention will now be explained, by way of illustration only.

Example 1

100 parts by weight of low density polyethylene (Yukalon YF-30, made by Mitsubishi Petrochemical), 10 parts by weight of azodicarbon-amide and 0.8 parts by weight of dicumyl peroxide are uniformly kneaded by a roll mill and are formed into cubic granules having a side of about 3 mm. 18 gms. of the kneaded granules 72 gms. of high density polyethylene powder (Nissan 6020P, 100 to 200 meshes, made by Nissan Chemical Industry), and 0.7 gms. of azodicarbon-amide were mixed together in a blender. Then the mixture was placed in a steel mould of 220×50×25 mm and was heated and foamed for 45 minutes by hot air at 300°C while the mould was rotated at a speed of 4 revolutions per minute. The foamed material thus obtained had a slightly foamed strong surface layer of a uniform thickness of about 4 mm and a well foamed core at the inside, and showed excellent compression strength and flexile strength.

Example 2

Granular and powdered plastics materials and a mould similar to those used in Example

1 were used, and by varying the weight ratio of the two kinds of plastics, moulded articles expanded to about 3 times the volume of the starting materials were produced, the thickness of surface layers being varied. The results of measurement of the thickness of the surface layers and bending elasticity are shown in Table 1, from which it may be seen that the larger the thickness, the greater is the bending elasticity, and further that the bond between the surface layer and foamed core is very strong

TABLE 1

Thickness of Surface Layer (mm)	Bending Elasticity (kg/cm^2)
0.5	1,100
1.0	1,630
1.5	2,400
2.0	3,260
2.5	4,130

Example 3

100 parts by weight of low density polyethylene, 10 parts by weight azodicarbonamide, and 0.3 parts by weight of dicumyl peroxide were kneaded uniformly by a roll mill and formed into cubic granules with a side of about 5 mm (A). 100 parts by weight of epoxy resin (Epicoat 828 made by Shell), 29 parts by weight of dipropyrene glycol, 44 parts by weight of pyromellitic acid anhydride, and 20 parts by weight of polyethylene glycol with a molecular weight of 3,000 were mixed for 3 hours at 60°C and the resultant product was cooled and pulverised into a powder having such particle size of 100 mesh or smaller (B).

25 gms. of the granules (A) and 75 gms. of the powder (B) were placed in a mould of 220×50×25 mm. and were heated and foamed for 60 minutes by hot air at 320°C while being rotated at a speed of 20 revolutions per minute. The foamed articles thus obtained had a uniform surface layer of about 3 mm in thickness, and furthermore had a harder surface layer and higher flexile strength than those of foamed articles made entirely of thermoplastic resin. They had sufficient resistance to deformation under a load at 100°C.

Example 4

Low density polyethylene granules (diameter about 3 mm.) containing a cross-linking agent and a foaming agent, high density polyethylene powder (MI.5) which passes through a 100 mesh screen, and asbestos (grade 7M in Canadian grade) subjected to 3 hours drying at 400°C, were mixed with the ratio shown in Table 2, then fed into a rectangular parallelepiped mould, 25 mm. thick, 50 mm. wide, 215 mm. long, and were heated for 30 minutes by hot air at 290°C while being rotated at a speed of 5 r.p.m. Thereafter the mould was cooled by water and such foamed shaped articles of about 3 times the volume of the starting materials and having a skin layer of uniform thickness were obtained. The moulded articles thus obtained had an inner core of 11 times the volume of its unfoamed constituent materials, and a large portion of the asbestos was contained in the 2 mm. thick skin layer which was not foamed. For comparison, instead of the above mentioned low density polyethylene granules, low density polyethylene powder passing through 100 mesh was used, together with cross-linking agent and foaming agent in the same ratios, and foamed articles with uniformity throughout their structure were moulded. The bending elasticity of the moulded articles thus obtained was measured by a 3 point load of span distance of 200 mm. The results are shown in Table 3 below.

TABLE 2 (Example)

	Low Density PE Granules (Containing cross-linking agent and foaming agent) gms.	High Density PE Powder gms.	Asbestos gms.	Bending Elasticity kg/cm^2
No. 1	18.4	66.2	7.4	3,100
No. 2	18.4	58.9	14.7	4,000

TABLE 3 (Comparison)

	Low Density PE Powder (Containing cross-linking agent and foaming agent) gms.	High Density PE Powder gms.	Asbestos gms.	Bending Elasticity kg/cm^2
No. 1	18.4	66.2	7.4	1,100
No. 2	18.4	58.9	14.7	1,200

It can be seen from the above results that when such powder form reinforcing material as asbestos is used, the reinforcing material will be gathered in the skin layer. Thus the object of the present invention can be more effectively achieved.

Example 5

Using the same foamable granules as in Example 1, sheets of 2 mm. thickness were moulded by an extruder. Then 1 mm. thick sheet of high density polyethylene was heated and, after heating, was laminated with the above mentioned first sheet. This composite sheet was cut into cubes having a side of about 3 mm. long. The foamed shaped articles produced from the above together with the powdered plastics material which is almost same as that used in Example 1 under the same production conditions, had very strong compressive strength because they contained layers of unfoamed high density polyethylene, being stretched into a skeleton-like structure, throughout the foamed inner core.

Example 6

20 grams of granules of a copolymer of ethylene and vinyl acetate having a side length of about 1 mm. were added to the powder material used in Example 1 and the mixture was heated and foamed under the same production conditions as for Example 1. A moulded article having a three layer structure of polyethylene, ethylene-vinyl acetate copolymer, and cross-linked polyethylene was obtained.

Example 7

100 parts by weight of ethylene vinyl acetate copolymer, 5 parts by weight of azodicarbonamide, and 1.2 parts by weight of dicumyl peroxide were sufficiently kneaded by a roll mill, then pulverised to obtain powder under 50 mesh. 100 gms. of the granules used in Example 1 were added to 100 gms. of this powder and the mixture was placed in a mould made of steel plates, having an uneven inner surface, intended to give rise to depressions on the surface of the moulded article of $100 \times 300 \times 50$ mm. size, and the mould was heated and foamed for 30 minutes by steam at a steam pressure of 12 kg/cm^2, while being rotated. The moulded article obtained was foamed to a volume about 7 times greater than that of the starting materials, and it had on its surface depressions, being exact reproductions of the inner surface of the mould, and also showed great friction resistance of its surface.

Example 8

5 grams each of rigid PVC, polystyrene, and nylon, each of which being cut to have a size of about 3 mm., was added to the powder material shown in Example 1, and was foamed under the exactly same conditions as shown in Example 1. The moulded article thus obtained had a smooth surface, and the rigid PVC, polystyrene and nylon were mixed in the inner core of the same.

Example 9

The material shown below was mixed together and was placed in a mould for a pallet, heated for 70 minutes by hot air of 350°C, while being rotated at 0.5 r.p.m., and then was rapidly cooled by a shower. A pallet with a shape shown in Figure 1 of the accompanying drawings, with a density of 0.5 gms/cm^3, was obtained.

High density PE (MI 2, 100 to 200 mesh)	15.3 kg
Low density PE (MI 1, 30 to 50 mesh)	4.0 kg
Azodicarbon-amide	0.2 kg
Foamable granules (diameter 6 mm., length 6 mm.)	2.1 kg
which consist of	
	parts by weight
High density PE	50
Low density PE	50
Azodicarbon-amide	10
Dicumyl peroxide	0.8

This pallet had a strong surface layer and the amount of deflection as measured by JIS-Z-0602 was as shown in curve A of Figure 2 of the accompanying drawings, thus being very strong. This pallet passed the drop test and compressive strength test set by JIS-Z-0602, (Japanese Industrial Standard).

On the other hand, a pallet obtained by the same method as shown above with the material obtained by mixing the high density polyethylene powder, low density polyethylene powder, and azodicarbon-amide with an extruder for forming the same to a shape of 6 mm. diameter and 6 mm. length, then mixing the same with cross-linkable pellets of the same shape, did not have a skin sufficiently formed, with its strength being lower as shown by the curve B in Figure 2.

Example 10

Metal mould inserts made of steel plate, and having the shape as shown in Figures 3(a) and 3(b) of the accompanying drawings were inserted at both ends of a mould for making the pallet shown in Figure 1, and a pallet was produced under the same conditions as those described in Example 9. The position of this metal insert was so controlled that it came to the position of 3 mm. from the surface layer of the pallet, and the major part of the metal insert was positioned substantially at the surface layer portion of the

pallet. The pallet thus obtained had a portion for receiving the tines of a forklift reinforced by these metal inserts. Thus it was very strong against impact and had low deflection as shown by the curve C in Figure 2.

Example 11

100 parts by weight of polypropylene with a Melt Index of 1.3 (Commercial Name Mitsubishi Noblen), 5 parts by weight of azodicarbon-amide, and 5 parts by weight of polybutadiene (Commercial name Nippol BR 1220 made by Nippon Zeon) were uniformly kneaded by a roll mill to form granules having a side of 3 mm. 70% by weight of polypropylene powder containing a small amount of foaming agent was mixed into 30% by weight of the above mentioned granules and 90 gms. of this mixture were placed in a mould made of steel plate, $22 \times 5 \times 2.5$ cm. and was heated and foamed for 45 minutes by hot air at 300°C while being rotated at a speed of 10 r.p.m. The foamed article thus obtained had a strong surface layer of uniform thickness of about 2 mm., as shown in Figure 4 of the accompanying drawings, and it was very strong.

Example 12

72. gms. of PVC powder (100 mesh or smaller) and 1 gm. of azodicarbon-amide were added to 8 gms. of the cross-linkable foamable granules used in Example 9 and the mixture was placed in a mould made of aluminium having an inside volume of 240 ml., and was heated for 15 minutes, while being rotated at a speed of 8 r.p.m., by steam under a pressure of 10 kg/cm². The moulded article obtained by water cooling the above had an almost uniform surface layer of PVC as shown in Figure 5 of the accompanying drawings and had flame retardant characteristics. and the bonding between the cross-linked PE and PVC was satisfactory.

A moulded article obtained by using 52 gms. of PVC powder, and 20 gms. of ethylene-vinyl acetate copolymer having a side of about 1 mm. (instead of the 72 gms. of PVC mentioned above) and foaming the same in the above manner had the ethylene-vinyl acetate copolymer situated at the centre of the PVC, and the bonding between the polyethylene and the PVC was very good.

Example 13

2 kg. of the cross-linkable granules used in Example 9 and 18 kg. of ABS powder (under 100 mesh) were placed in a mould made of steel plate for making the article having indentations as shown in Figure 6 of the accompanying drawings, the indentations having a size of $1000 \times 1000 \times 150$ mm., and these plastics materials were heated and foamed for 60 minutes at 330°C while being rotated at a speed of 1 r.p.m. Then the same was rapidly cooled to obtain the foamed composite moulded article. This moulded article had a uniform surface layer of ABS resin and had excellent bending elasticity. Further, the surface layer in the region of these indented portions was particularly strong, so that the deflection and compression strength of the portions were very good.

Example 14

50 parts by weight of high pressure PE, 50 parts by weight of medium pressure PE, 1 part by weight of dicumyl peroxide, and 5 parts by weight of azodicarbon-amide were kneaded by a roll mill and were formed into granules having one side of about 5 mm.

40 grams of medium pressure PE powder were added to 40 grams of said granules and the mixture was placed in a mould of $200 \times 50 \times 25$ mm. and was heated and foamed for 60 minutes at 250°C within a thermostat having a shaking apparatus, while being shaken in a horizontal direction with a stroke of 50 mm. at a speed of 60 strokes a minute. The foamed article thus obtained had a density of 0.35 gms./cm³, wherein a well foamed layer and a rigid and strong plastics layer were very rigidly bonded together.

WHAT WE CLAIM IS:—

1. A method for producing foamed composite articles, which method comprises: placing in a mould a) powdered plastics material the particles of which are less in size than 10 mesh, and b) granular plastics material the particles of which are greater in size than 10 mesh, which granular plastics material contains a foaming agent—the size of the granular plastics particles being at least 3 times that of the powdered plastics particles; rotating and/or vibrating the mould to separate said two kinds of plastics particles from each other; and heating the same.

2. A method as claimed in claim 1, in which the powdered plastics material has a particle size of 30 mesh, or a smaller particle size.

3. A method as claimed in either of claims 1 and 2, in which a powdered metal is first mixed with the powdered plastics material before this is placed in the mould.

4. A method as claimed in claim 3, in which the powdered metal is powdered aluminium.

5. A method as claimed in any of the preceding claims, in which the powdered plastics material contains a foaming agent, a flame retarding agent, an antioxidant, an ultra violet ray absorbing agent, and/or a reinforcing agent.

6. A method as claimed in claim 5, in which the foaming agent is azodicarbon-amide, and the reinforcing agent is asbestos.

7. A method as claimed in any of the preceding claims, in which the powdered plastics

material is polypropylene, high density polyethylene, nylon, ABS resin, polyvinyl chloride resin, a polycarbonate, or a phenolic resin.

8. A method as claimed in any of the preceding claims, in which the granular plastics material has a particle size of 5 mesh, or a larger particle size.

9. A method as claimed in any of the preceding claims, in which the granular plastics material is low density polyethylene, rigid PVC, polystyrene, and/or nylon.

10. A method as claimed in any of the preceding claims, in which the granular plastics particles are formed by taking a foamable plastics material and laminating it with, or covering it by extrusion with, a non-foamable plastics material, or a plastics material capable of foaming only from one to three times its unfoamed volume, and then dividing this composite material into granules of a size greater than 10 mesh.

11. A method as claimed in any of the preceding claims, in which the size of the granular plastics particles is at least ten times that of the powdered plastics particles.

12. A method as claimed in any of the preceding claims, in which the powdered plastics material has a higher melting point than has the granular plastics material.

13. A method as claimed in any of the preceding claims, in which, in addition to the powdered plastics material and the granular plastics material, an intermediate-size plastics material is placed in the mould, to produce foamed composite articles having three or more layers.

14. A method as claimed in any of the preceding claims, in which hollow glass spheres, light-weight aggregate, wood chips and/or metal chips are placed in the mould together with the plastics materials.

15. A method as claimed in any of the preceding claims, in which, in addition to the granular plastics material defined in any of claims 1 or 8 to 10, there is placed into the mould further granular plastics material the particles of which are greater in size than 10 mesh, which further granular plastics material is non-foamable or is capable of foaming only to from one to three times its unfoamed volume.

16. A method as claimed in any of the preceding claims, in which the mould is rotated slowly so as to produce substantially no centrifugal effect.

17. A method as claimed in claim 16, in which the speed of the fastest moving portion of the mould is 15 metres/minute or slower.

18. A method as claimed in claim 17, in which the speed of the fastest moving portion of the mould is from 0.1 metres/minute to 5 metres/minute.

19. A method as claimed in any of the preceding claims, in which the mould and the plastics material contained therein are heated by steam or hot air.

20. A method as claimed in any of the preceding claims, in which the mould is subsequently cooled either by placing the mould into water, or by spraying water onto the mould.

21. A method as claimed in any of the preceding claims, in which the mould is so formed as to provide depressed or indented portions on the surface of the foamed composite articles formed therein.

22. A method as claimed in any of these preceding claims, in which a reinforcing member is placed adjacent the inside mould wall, before the plastics material is placed in the mould.

23. A method for producing a foamed composite article as claimed in any of claims 1 to 22, and substantially as hereinbefore.

24. A foamed composite article, whenever prepared by a method as claimed in any of the preceding claims.

For the Applicant(s):
SANDERSON & CO.,
Chartered Patent Agents,
97, High Street,
Colchester, Essex.

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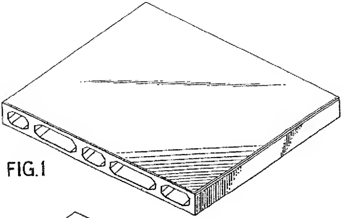


FIG.1

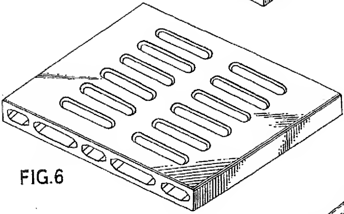


FIG.6

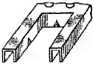


FIG.3(b)

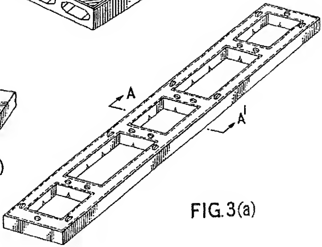
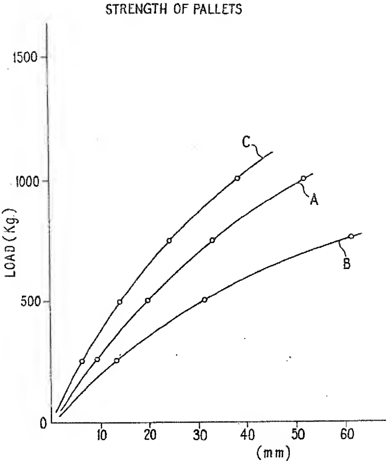


FIG.3(a)

FIG. 2


STRENGTH OF PALLETS
1500
1000
500
0
LOAD (Kg.)
10
20
30
40
50
60
(mm)
C
A
B

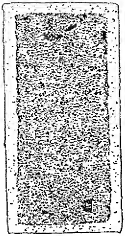


FIG. 4

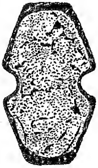


FIG. 5